# Isochronal Annealing of Radiation Damage in $\alpha$- and $\delta$-Pu Alloys

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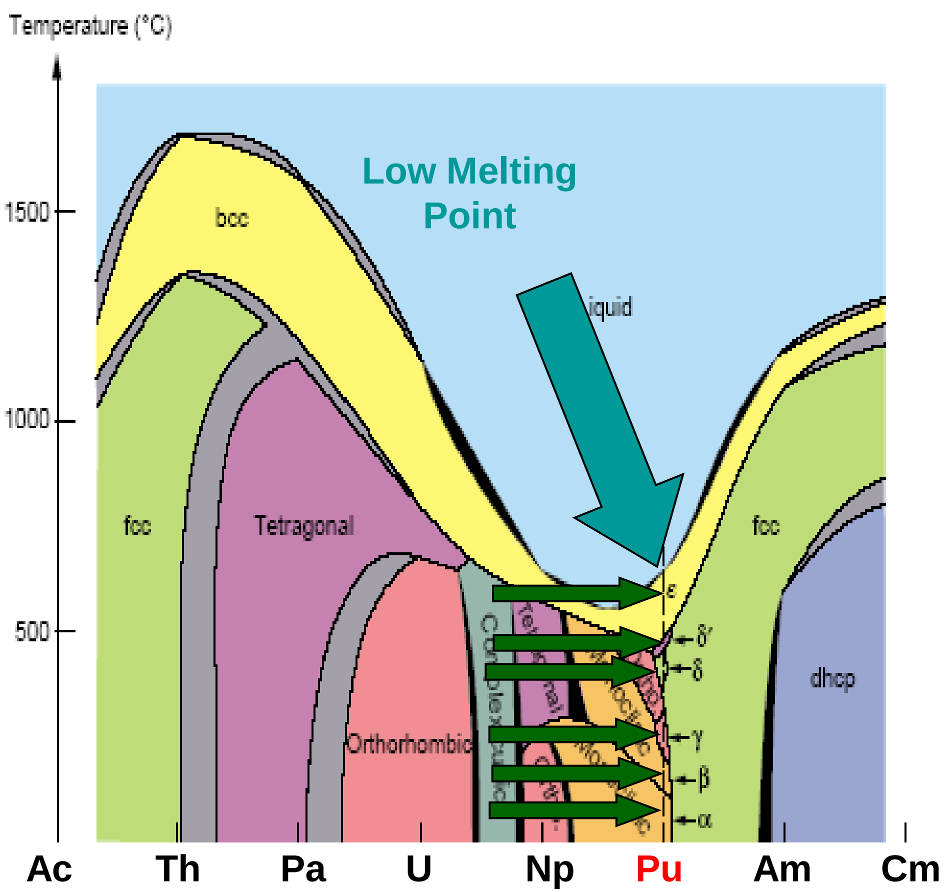
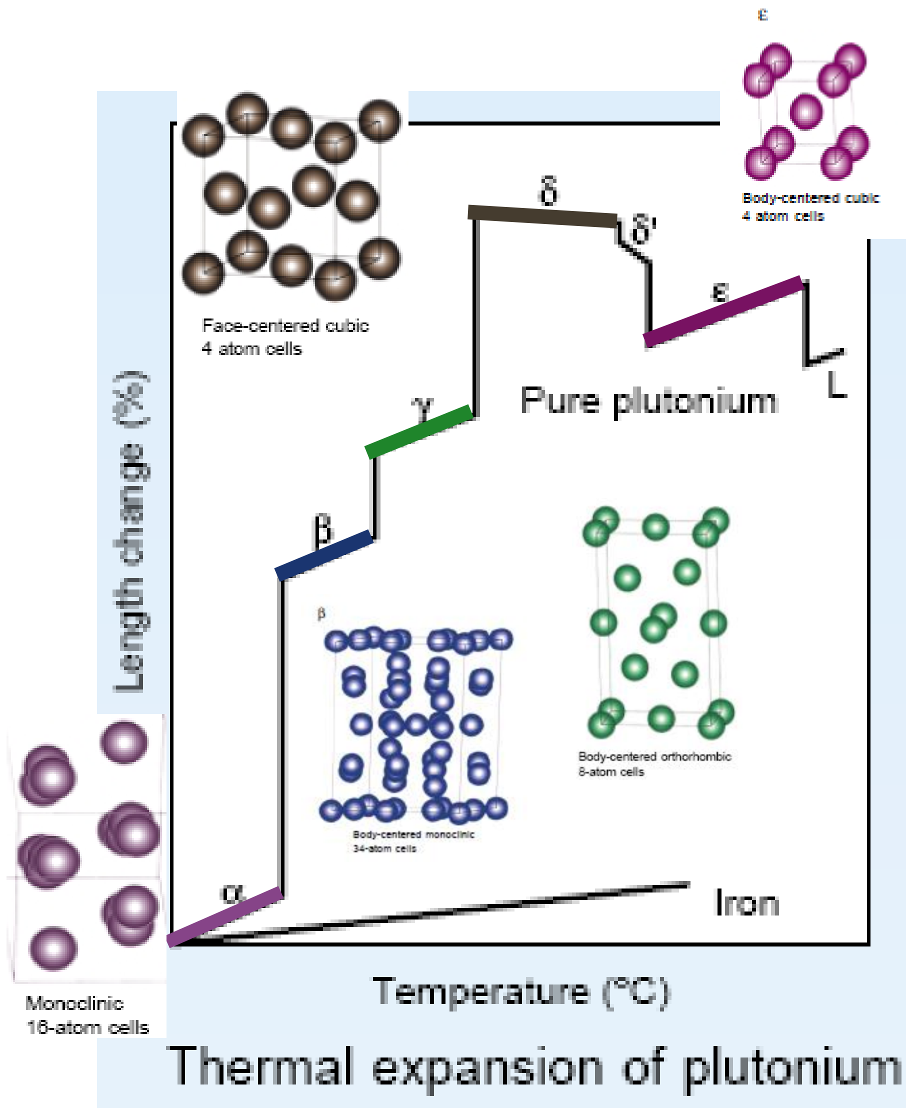
**LLNL-PRES-415419**

# Pure Plutonium has in many phases

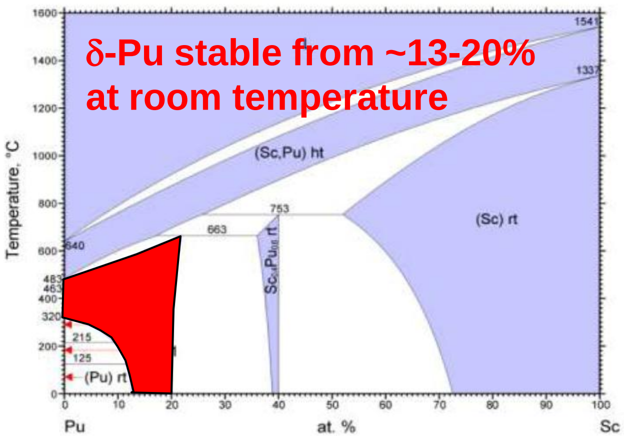


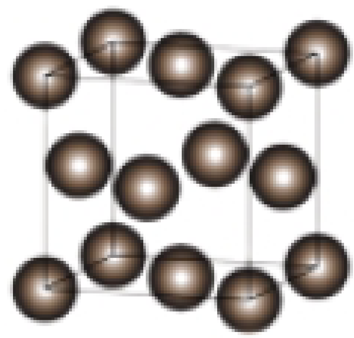

Los Alamos Science 26 (2000)

# There are multiple stabilizers for δ-Pu, most of which contract the lattice and work over only a limited concentration range

**Pu-Sc**




## δ-Pu



Face-centered cubic
4 atom cells

**Pu-Am**

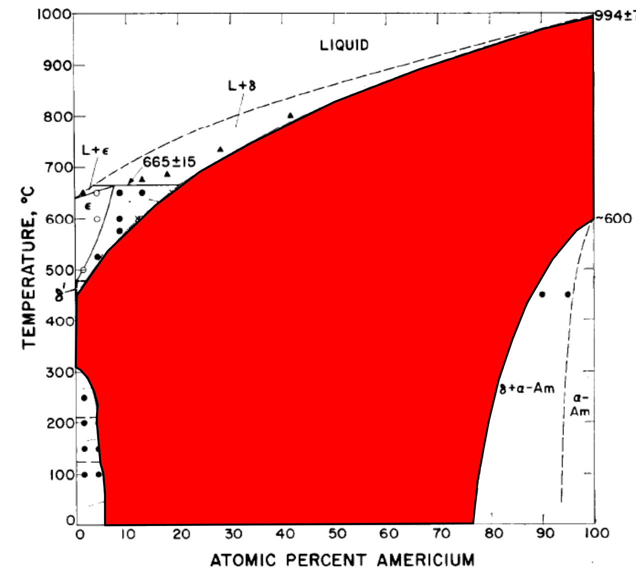
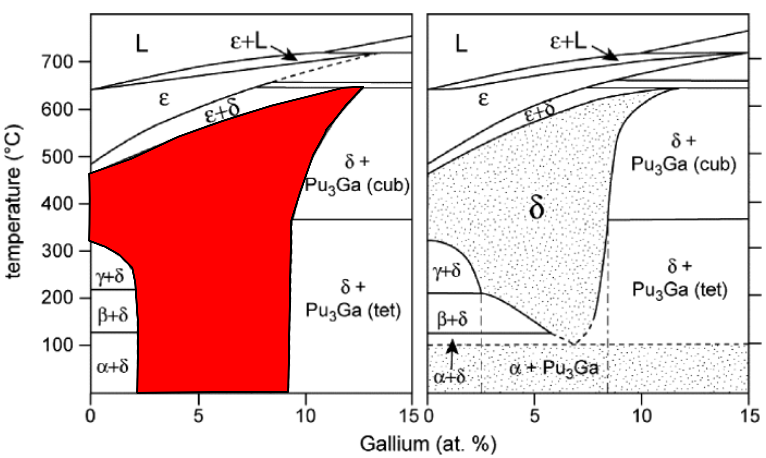


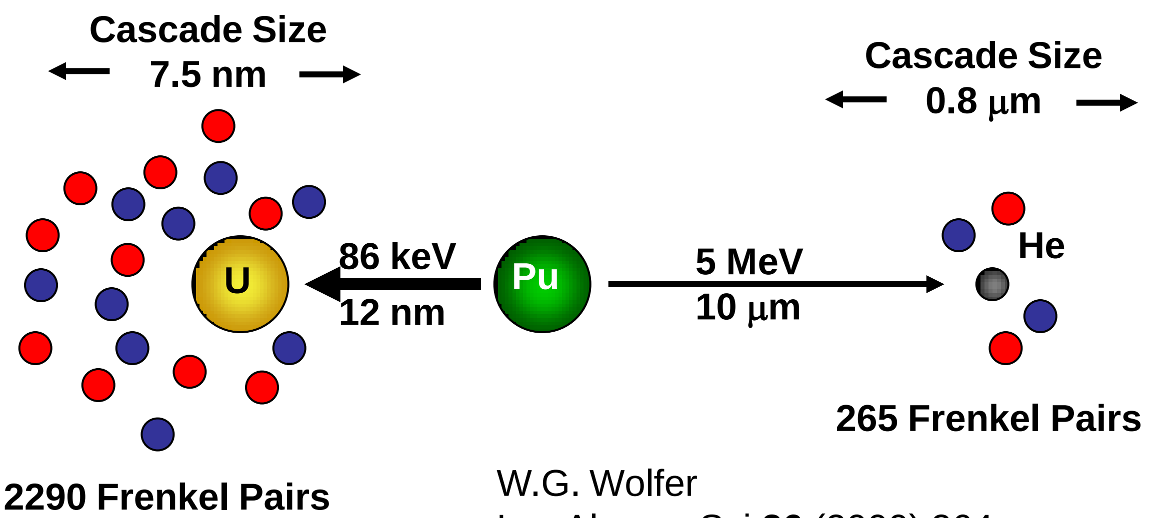

Fig. 2. The plutonium-americium phase diagram.

**Pu-Ga**



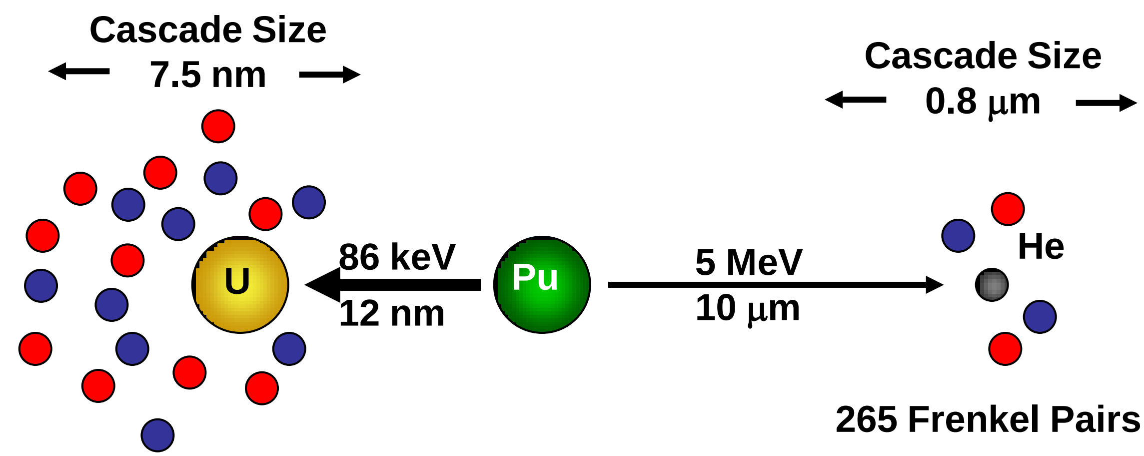

**PuAm alloys are stable over wide range of concentrations and the lattice parameter expands with [Am].**

# Self Damage in Plutonium occurs via α-decay




W.G. Wolfer
Los Alamos Sci **26** (2000) 264

# Self Damage in Plutonium occurs via α-decay

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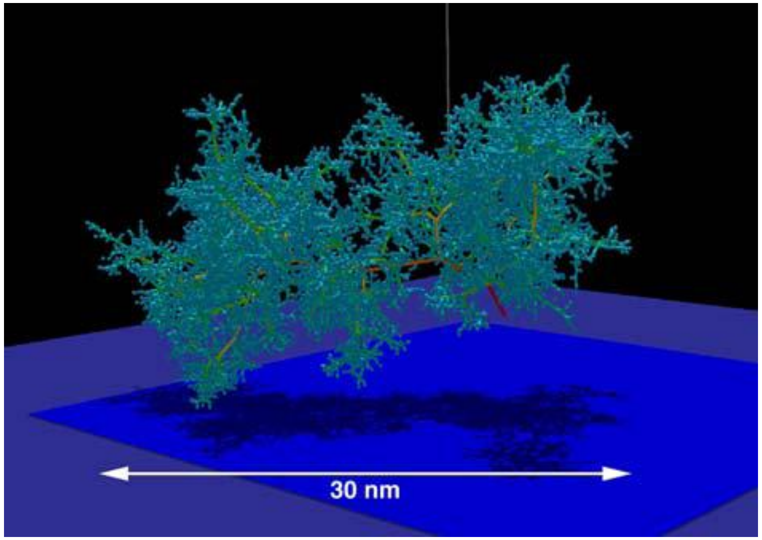


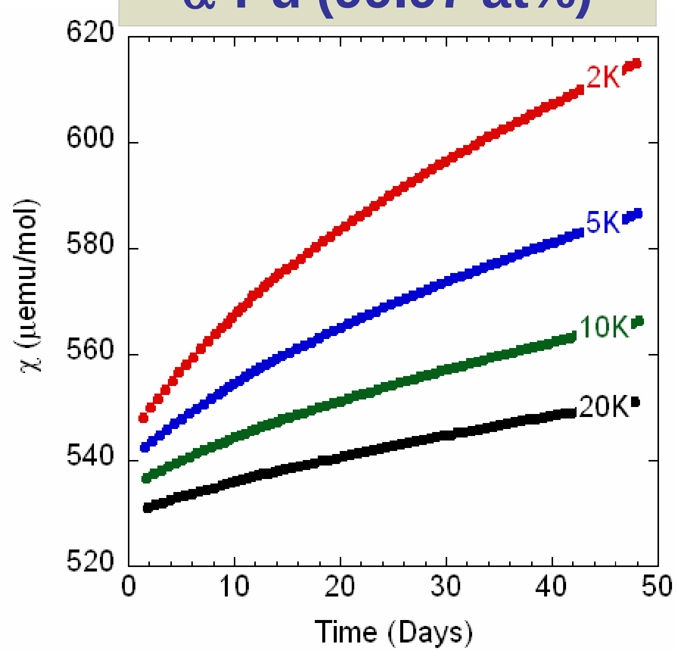

**Simulation of an 85 KeV collision cascade in δ-Pu at 600K**

Kubota et al J Comp-Aided Mater Des **14** 367(2007)

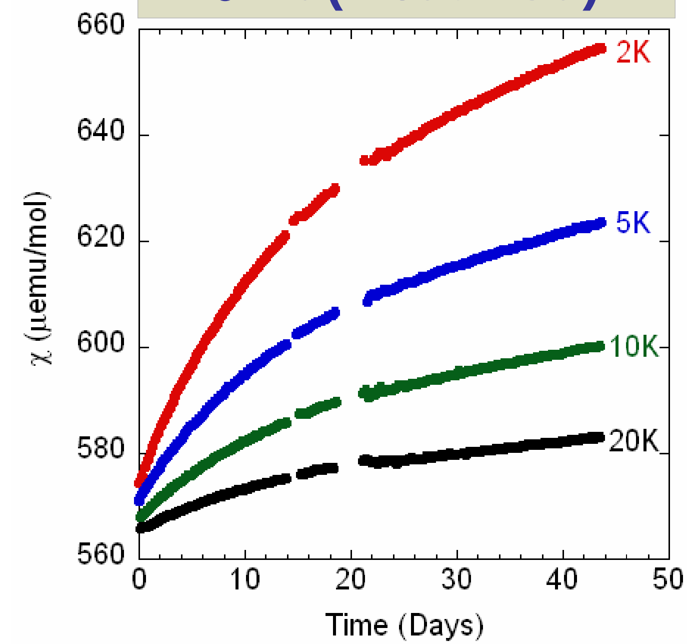
**More detailed calculations find a larger cascade size**

# Magnetic susceptibility of Pu increases with damage accumulation

### α-Pu (99.97 at%)




### δ-Pu(4.3at%Ga)




McCall *et al* Proc Nat Acad Sci 103 p17179 (2006)

$$\chi(t,T) = \chi_i(T) + \chi_{Bubble}(T)(1 - e^{-t/\tau}) + \chi'_D(T)\cdot t$$

**Initial Undamaged State**

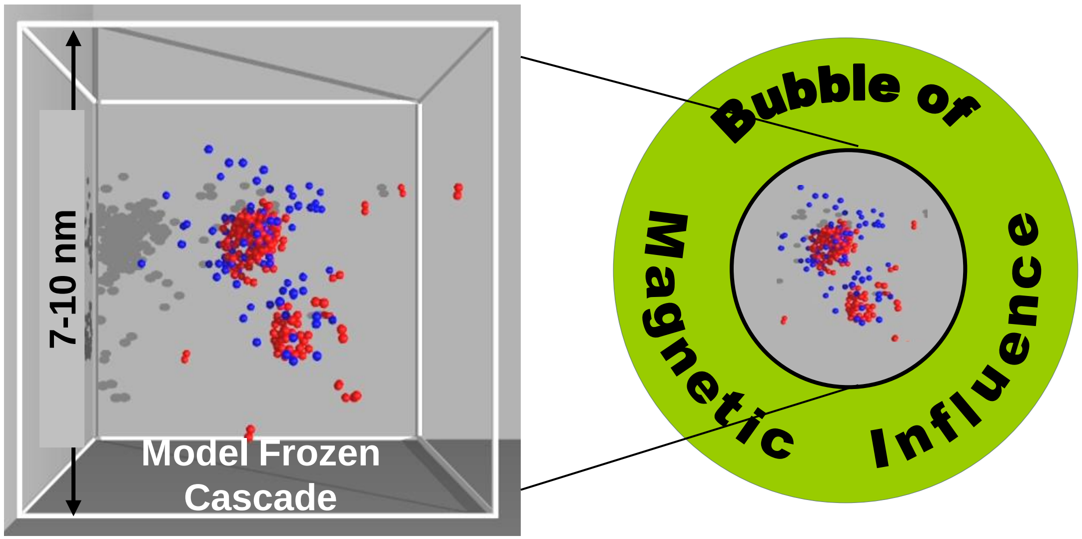
**Saturation Term**

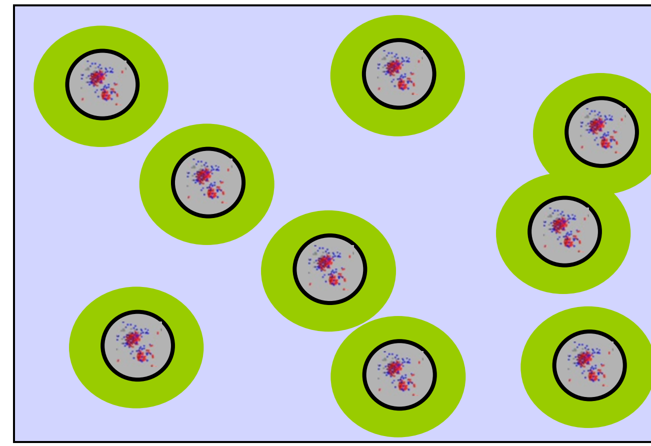
**Additional Disorder Term**

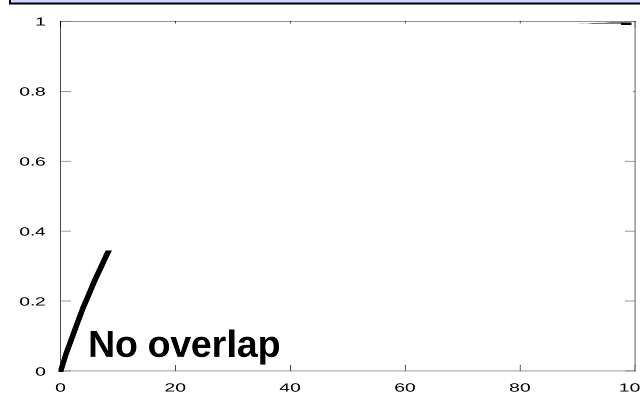
**τ is material, not T dependant**

# What does the time dependence reveal about radiation damage?

$$\chi(t,T) = \chi_i(T) + \chi_{Bubble}(T)(1-e^{-t/\tau}) + \chi_D(T)\,t$$





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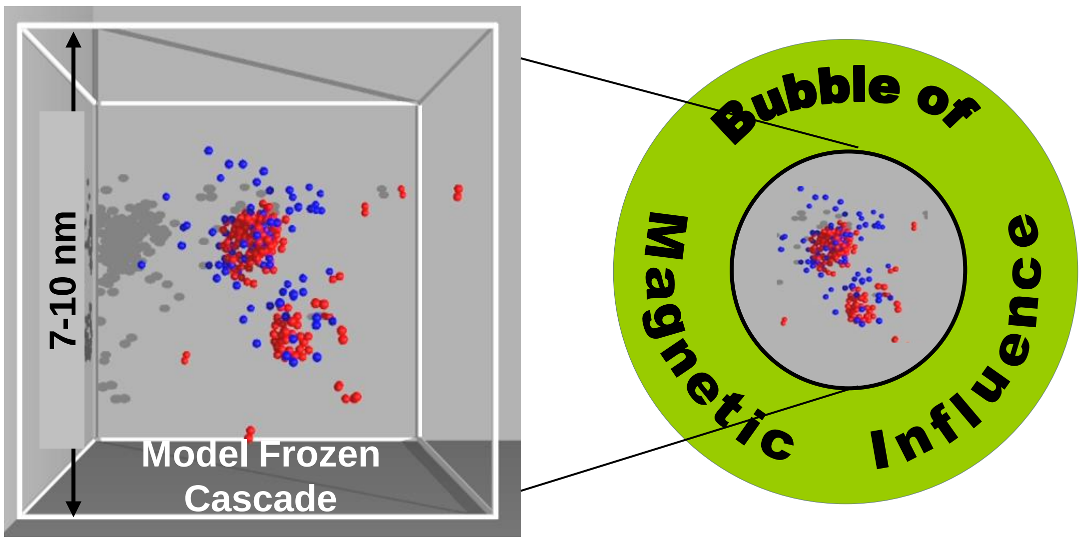
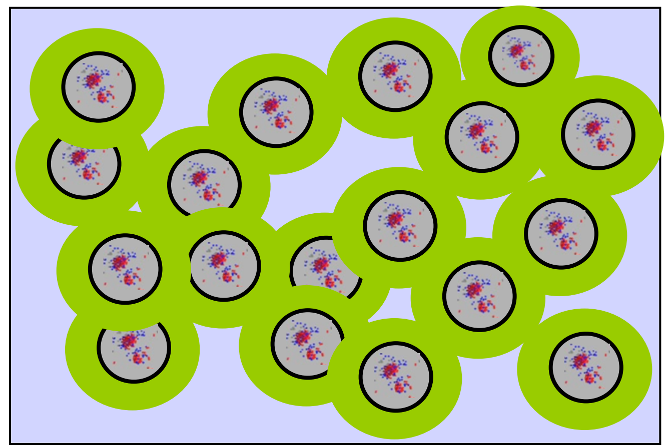
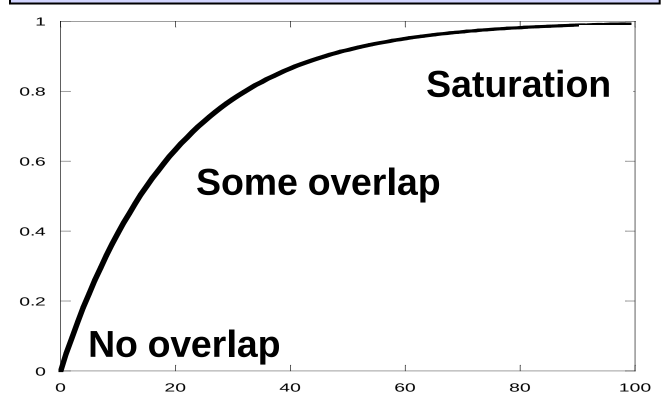
$$\chi(t,T) = \chi_i(T) + \chi_{Bubble}(T)(1-e^{-t/\tau}) + \chi_D(T)\,t$$

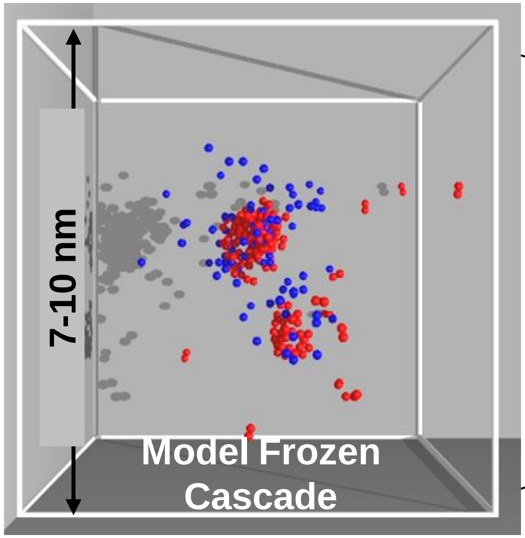


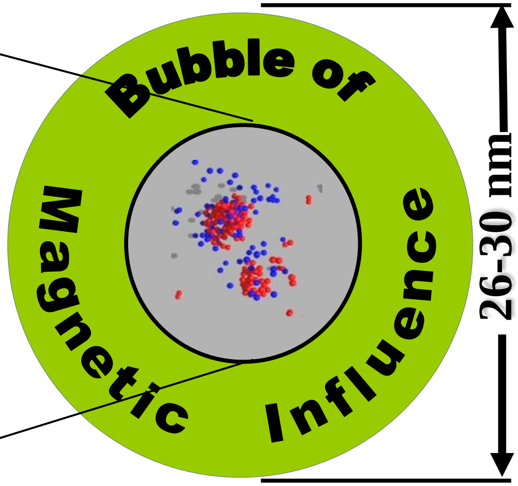



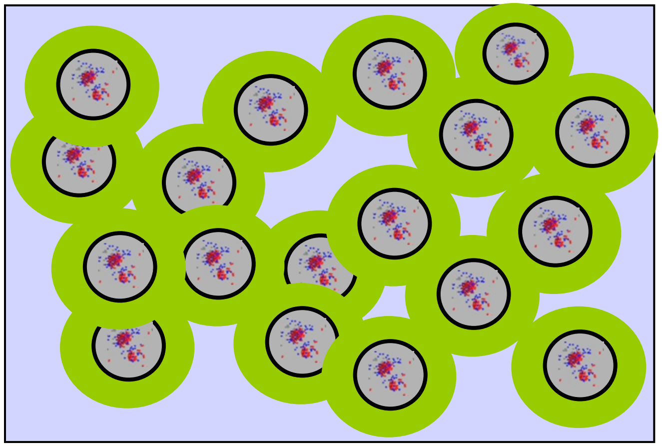


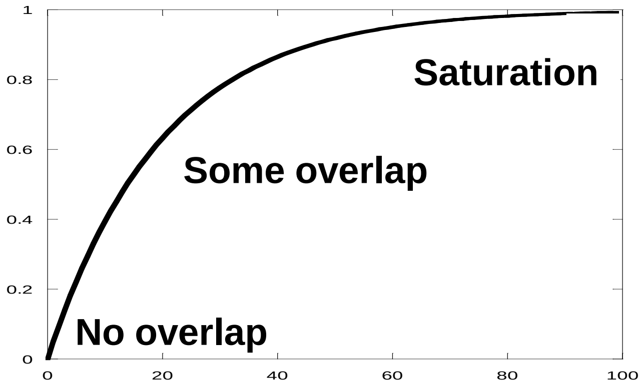
# What does the time dependence reveal about radiation damage?

$$\chi(t,T) = \chi_i(T) + \chi_{Bubble}(T)(1 - e^{-t/\tau}) + \chi_D(T)\,t$$






| | Days | Volume Influenced | Atom Equiv. |
|---|---|---|---|
| $\tau_\alpha$ | 15.8 | 9,800 nm$^3$ | 500,000 |
| $\tau_\delta$ | 11.5 | 13,600 nm$^3$ | 550,000 |

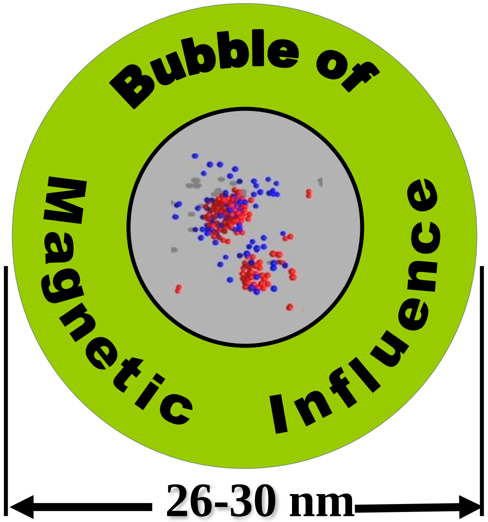
$\tau$=time constant
$\lambda_{Pu}$= alpha decay rate

$$\frac{1}{\tau} = \frac{V_{Bubble}}{V_{Sample}} \lambda_{Pu}$$

**The Contribution from self damage is spatially extended**

# The effects on the lattice due to the damage cascade are larger than initially thought

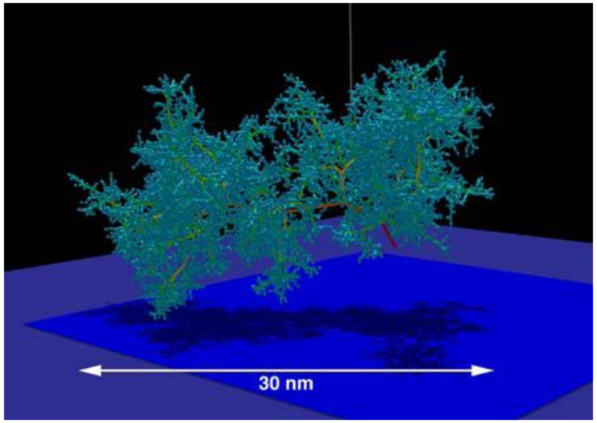
**Experimental Result**

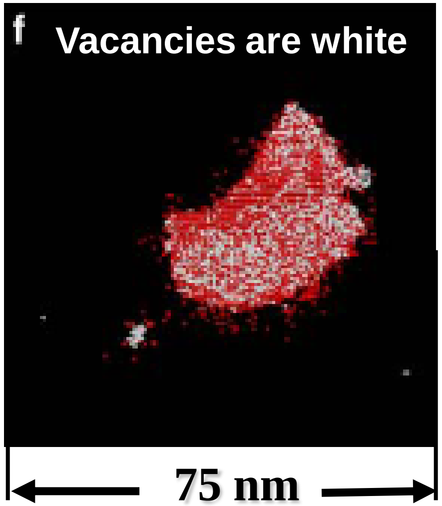



**Damage cascade frozen in at low temperature (< 30K)**

McCall *et al* Proc Nat Acad Sci **103** p17179 (2006)

**Theoretical Confirmation**



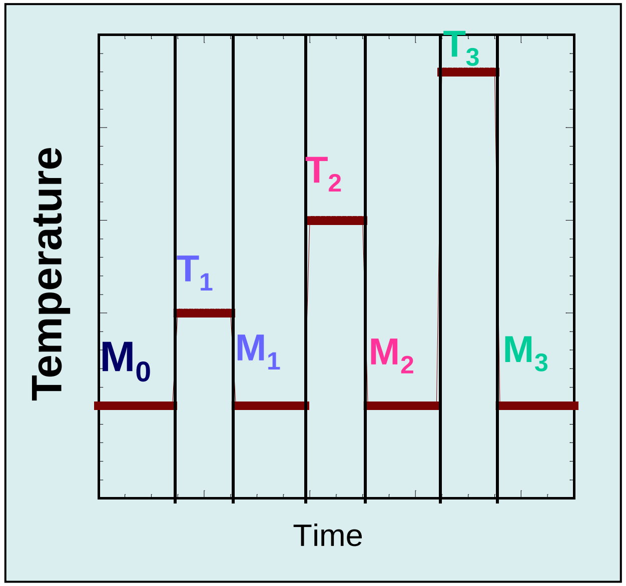

**Simulation of an 85 KeV collision cascade in δ-Pu at 600K**

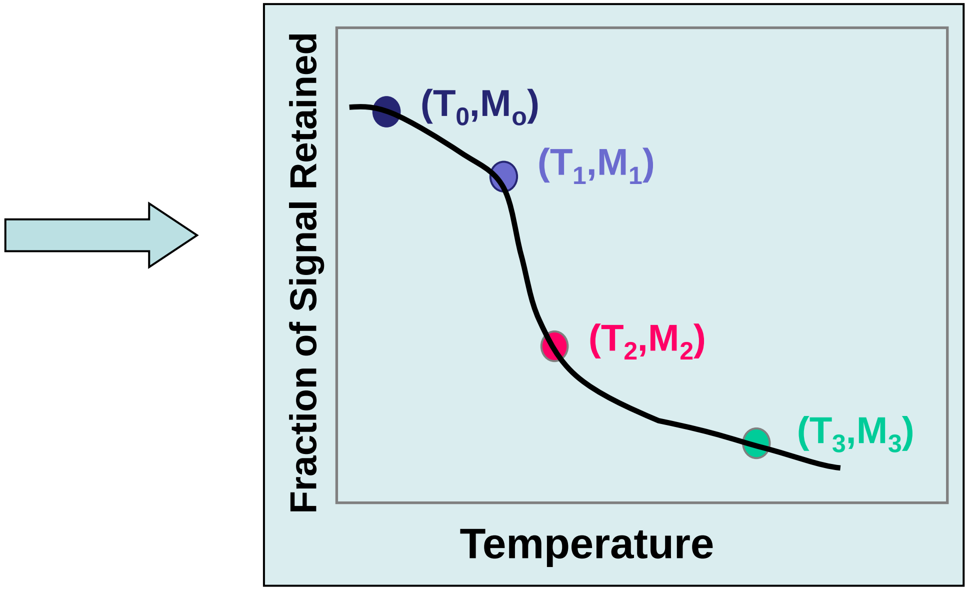
**Kubota et al J Comp-Aided Mater Des 14 367(2007)**

**Radiation damage in Pu is more complicated than a simple FCC estimate**

# Isochronal Annealing provides information about the temperature dependence of defects

**Accumulate damage at low temperature observable by a physically measureable property. Often this is resistance, but may include other properties such as magnetization.**




**The Fraction of Signal Retained depends on the sensitivity of the measurement to a particular type of defect.**

# Most isochronal annealing studies involve irradiation with electrons or protons, not heavy ions

**Damage cascades are be similar to those created by the $\alpha$ particle**

## Annealing Recovery Stages

I. Interstitials Migrate, Vacancy-Interstitial Close Pair Recovery
II. Release of Trapped Interstitials
III. Vacancy Activation
IV. Vacancy Clustering + Impurity Interactions
V. Vacancy Cluster Dissolution

**Electron irradiation of Pb**
**Measured by resistivity**

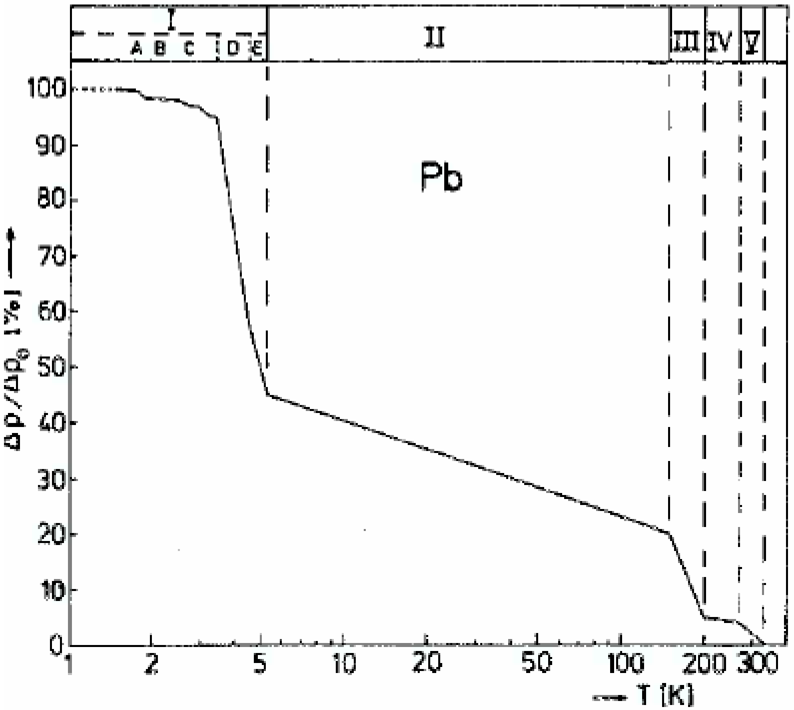
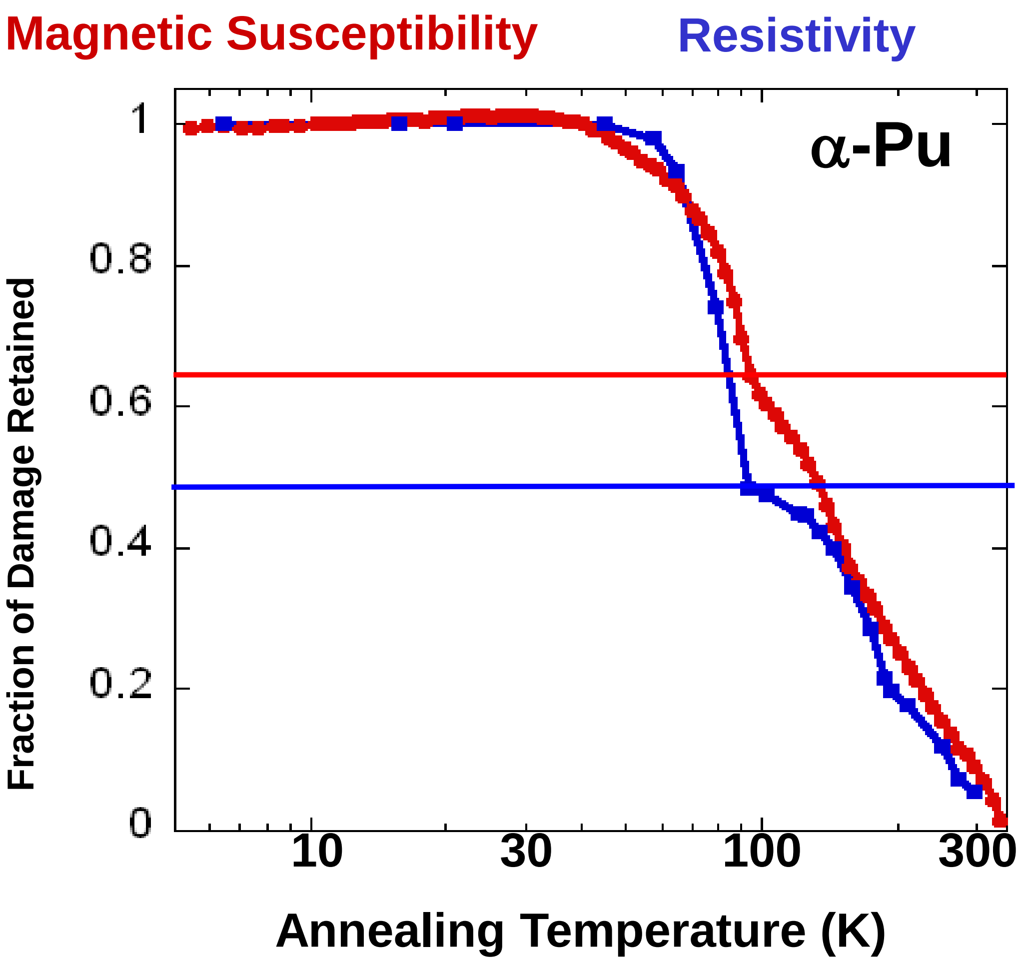



FIGURE 1 Schematic view of the recovery of lead after electron irradiation, indicating the main stages I to V.

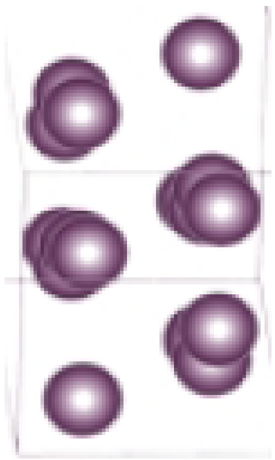
Schroeder and Shilling *Rad Eff* **30** (1976) 243

**Isolated Frenkel pairs in FCC metals have clear annealing curves**

# Isochronal annealing curves on “pure” plutonium are not quite as clear




Resistivity data from Wigley, Proc R Soc A **284** (1964)344



Monoclinic
16-atom cells

**Fraction of the damage annealed**

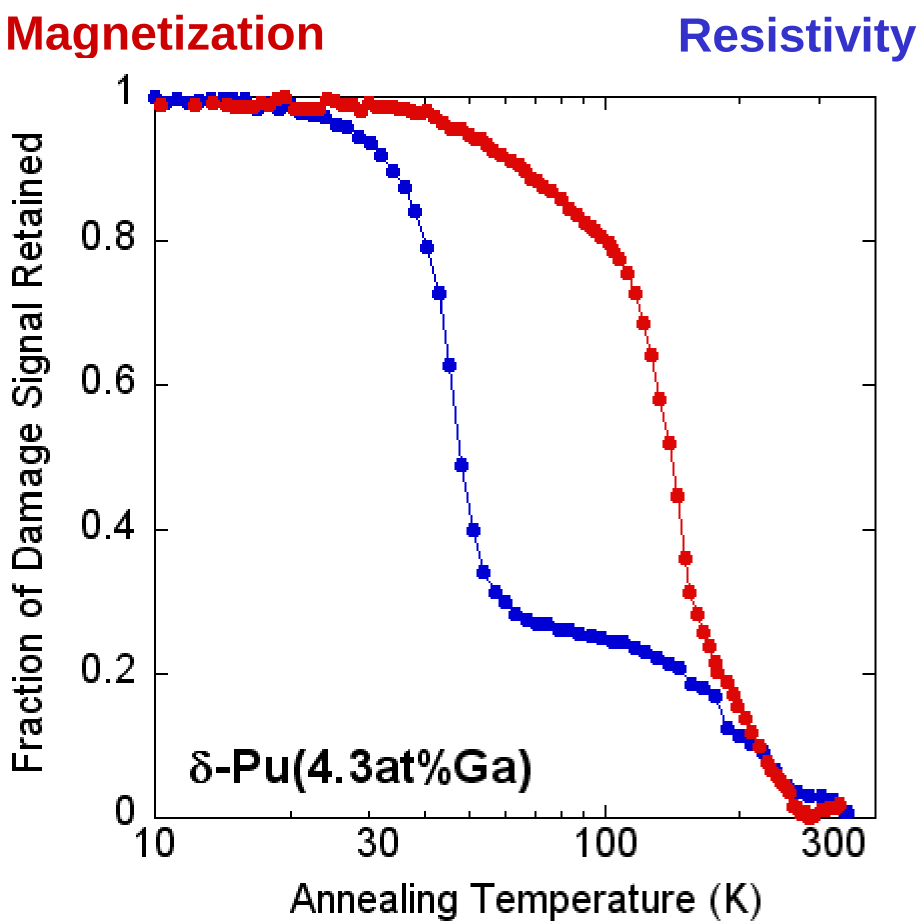
**Resistivity~50% at Stage I**

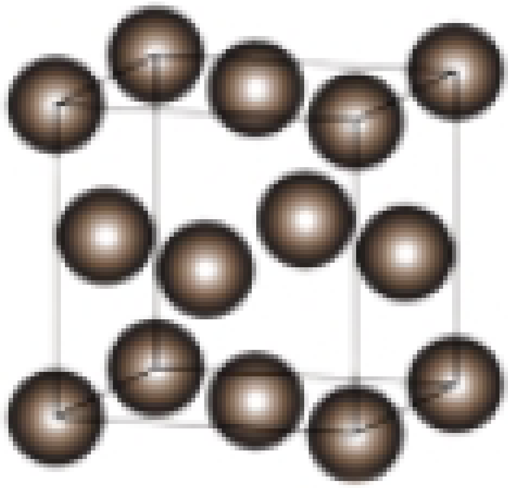
**Magnetization~33% at Stage I**

**The higher temperature annealing stages are not as obvious as in the case of Pb**

**The annealing stages of each occur at similar temperatures**

# Isochronal annealing using two different measurement techniques



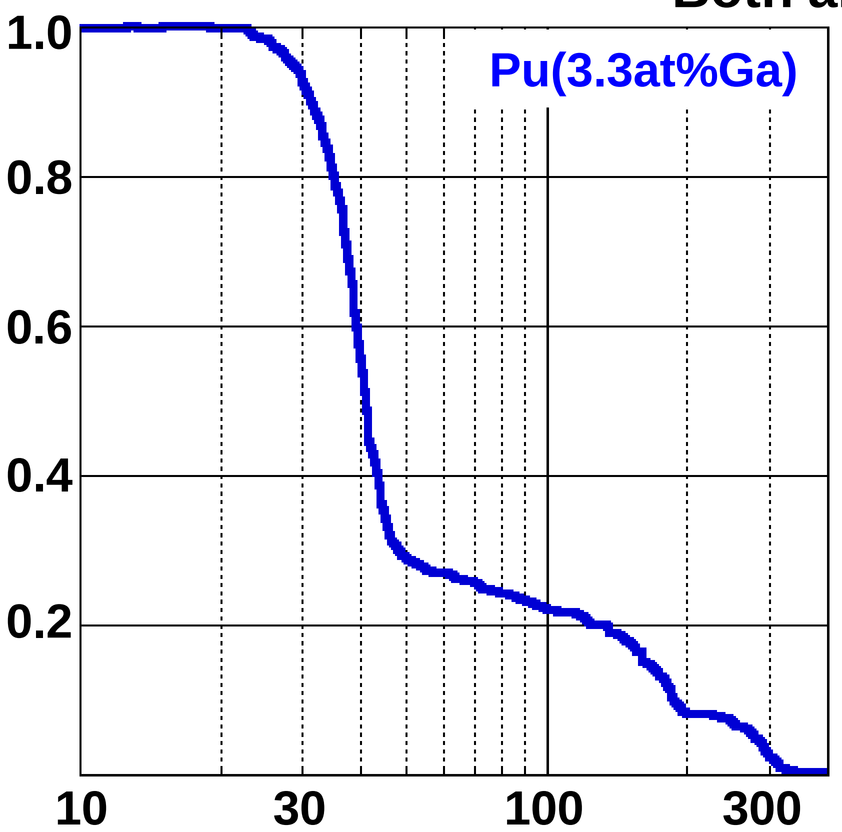
Face-centered cubic
4 atom cells

**Signal ≠ Damage**

**Very different annealing curve provide insight into different aspects of the damage cascade**

# Isochronal annealing of Pu(3.3at%Ga) shows distinctive annealing stages like lead

**Both are FCC metals**



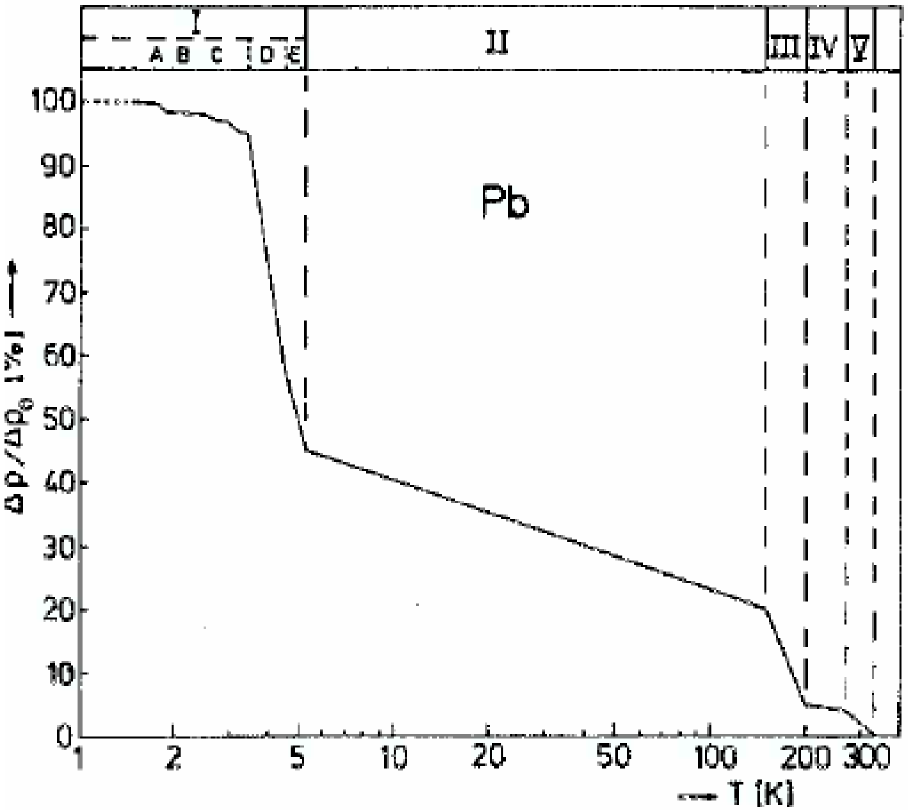
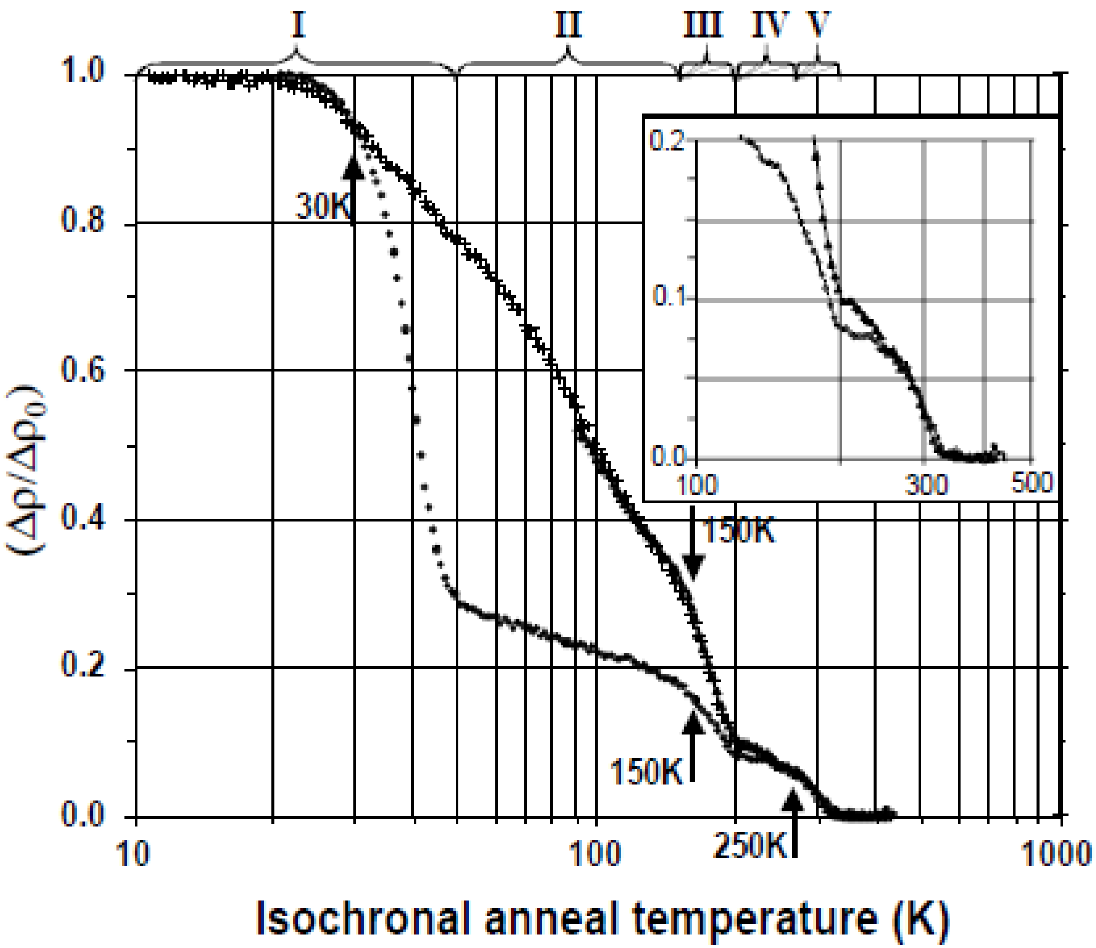




FIGURE 1 Schematic view of the recovery of lead after electron irradiation, indicating the main stages I to V.

**Majority of radiation damage from U recoil**

**Radiation damage from electron irradiation**

# Isochronal annealing of 3.8 MeV proton irradiation damage yields a different result at low temperatures



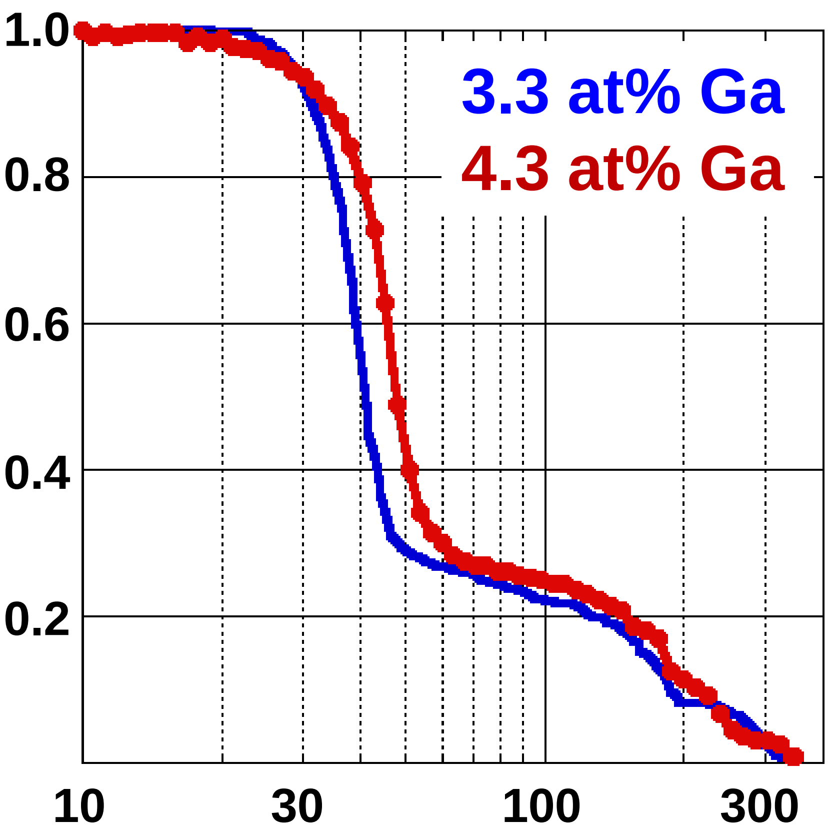

**Irradiation should predominately generate Frenkel pairs**

**Annealing curve more closely resembles a dirty metal**

**The "vacancy based" stages are similar for both cases**

**The difference in stage I behavior suggests self damage is not dominated by close pair recovery**

# Isochronal annealing of two resistivity specimens show similar overall results



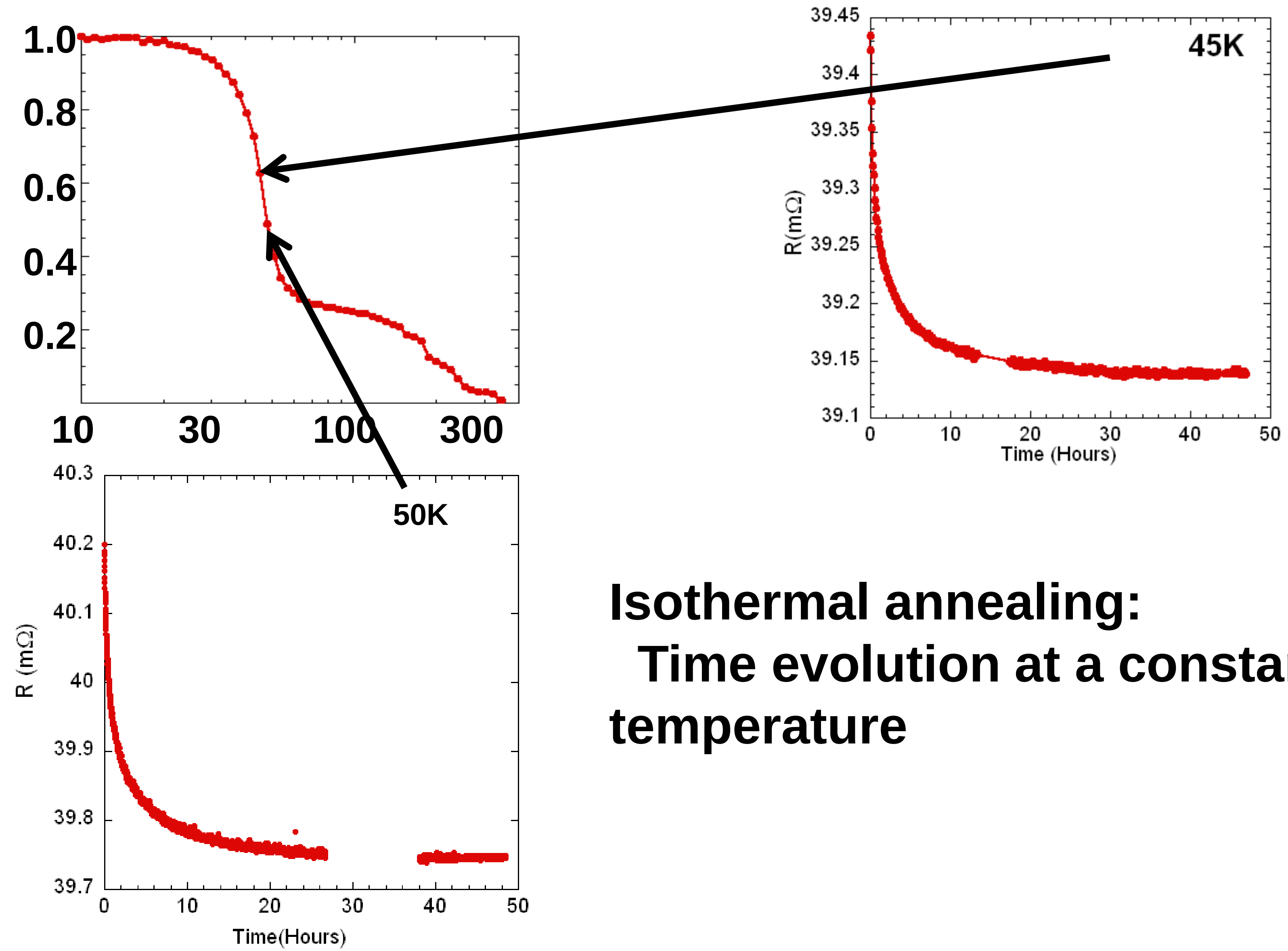

The annealing soak times were longer for the 4.3at% data.

One would expect this to show a lower onset temperature

Annealing stages at higher temperature are more smeared out than in the 3.3at%Ga data

**Stage I is "real" even though the specimen is highly impure**

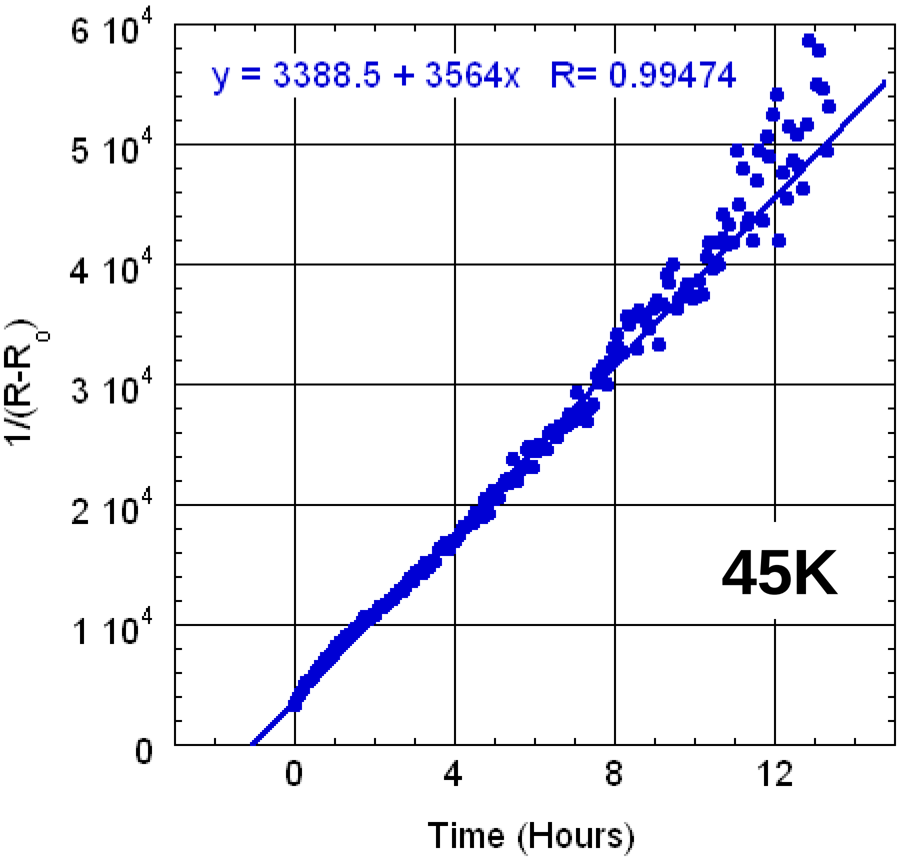
# Isothermal annealing at "Stage I" provides an opportunity to understand the details of the annealing stage

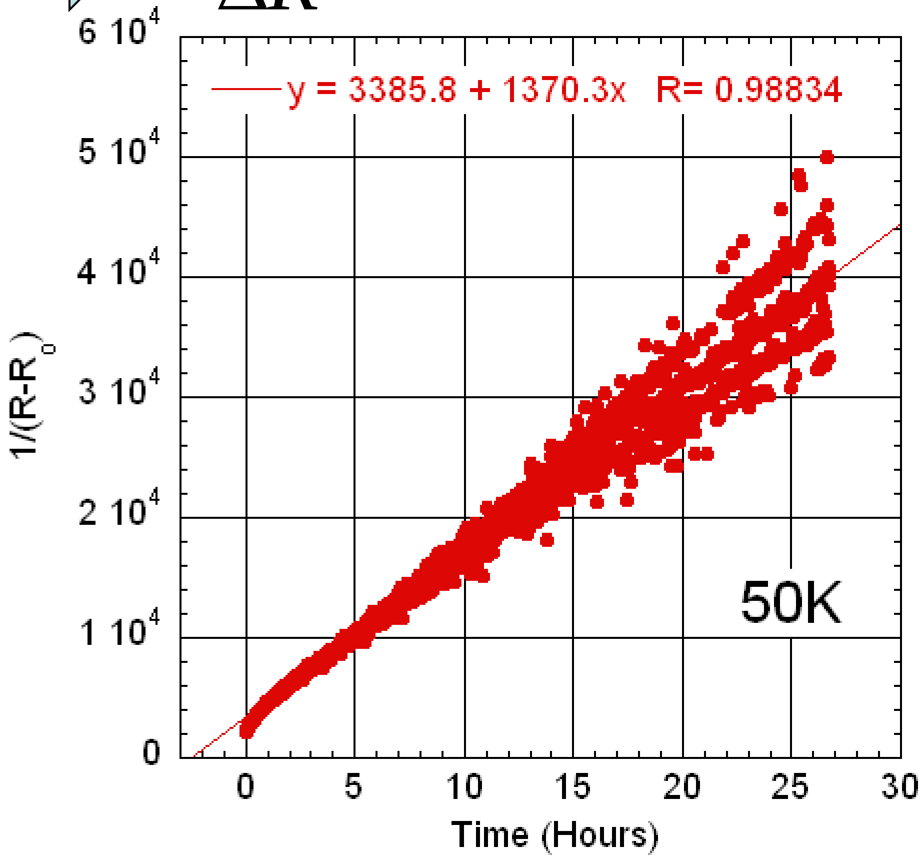



**Isothermal annealing:**
**Time evolution at a constant temperature**

# Is Stage I controlled by a simple chemical rate equation?

$$dp = -Kp^{\gamma}dt \quad \xrightarrow{\gamma=2} \quad \frac{1}{\Delta R} = C(t+M)$$

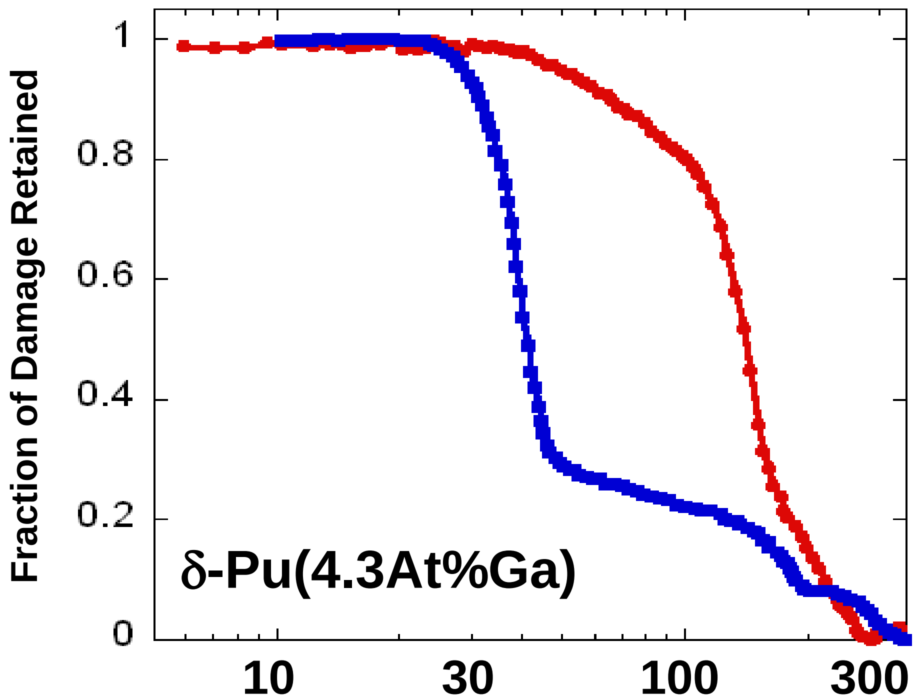



**$\gamma$=2 is reasonable thereby suggesting bimolecular kinetics**

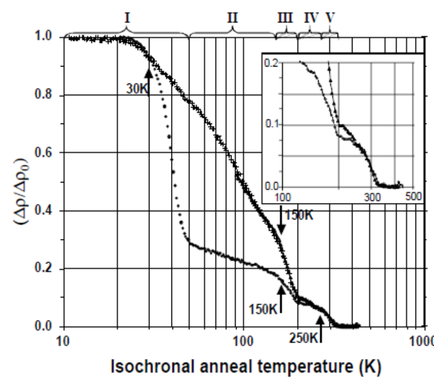
# Isochronal annealing with two separate techniques on δ-Pu(4.3at%Ga)

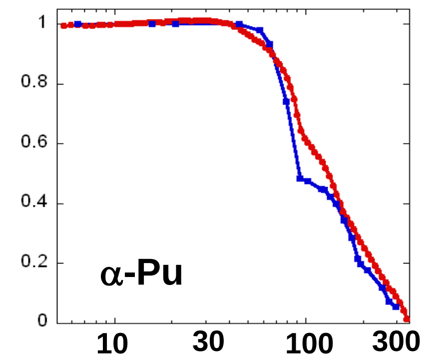
**Magnetization** **Resistivity**




**Stage I in the magnetization measurement is missing**

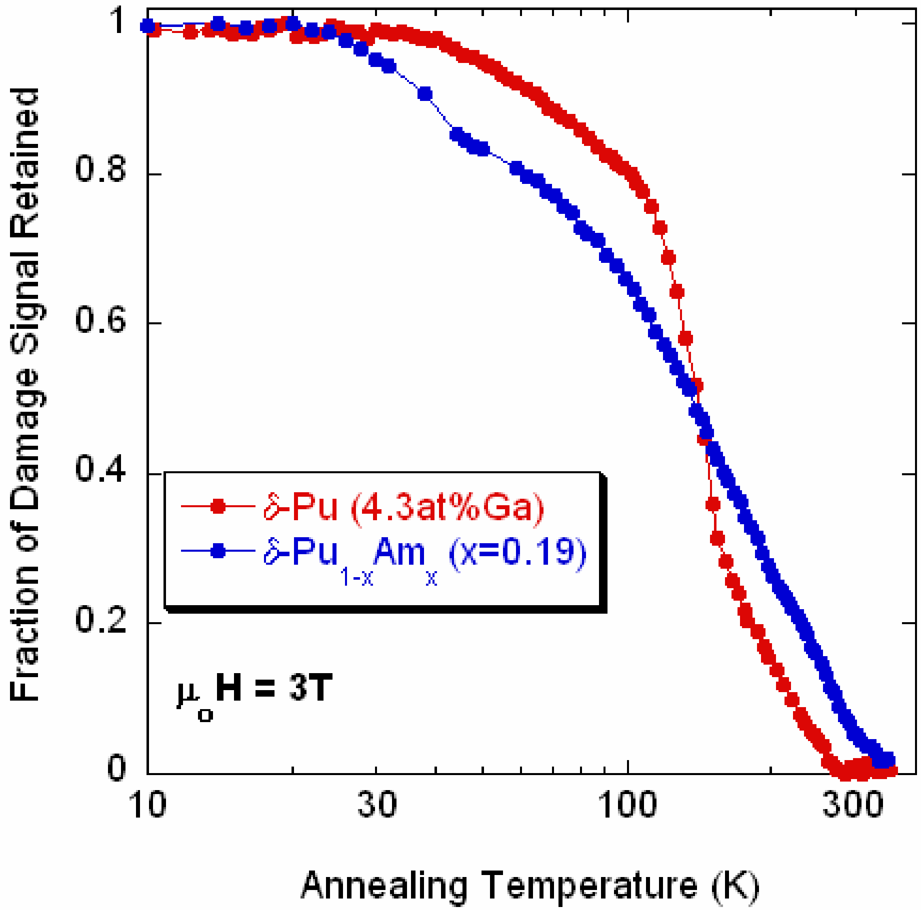
**Magnetization is sensitive to Stage III where vacancies are assumed to begin migration**



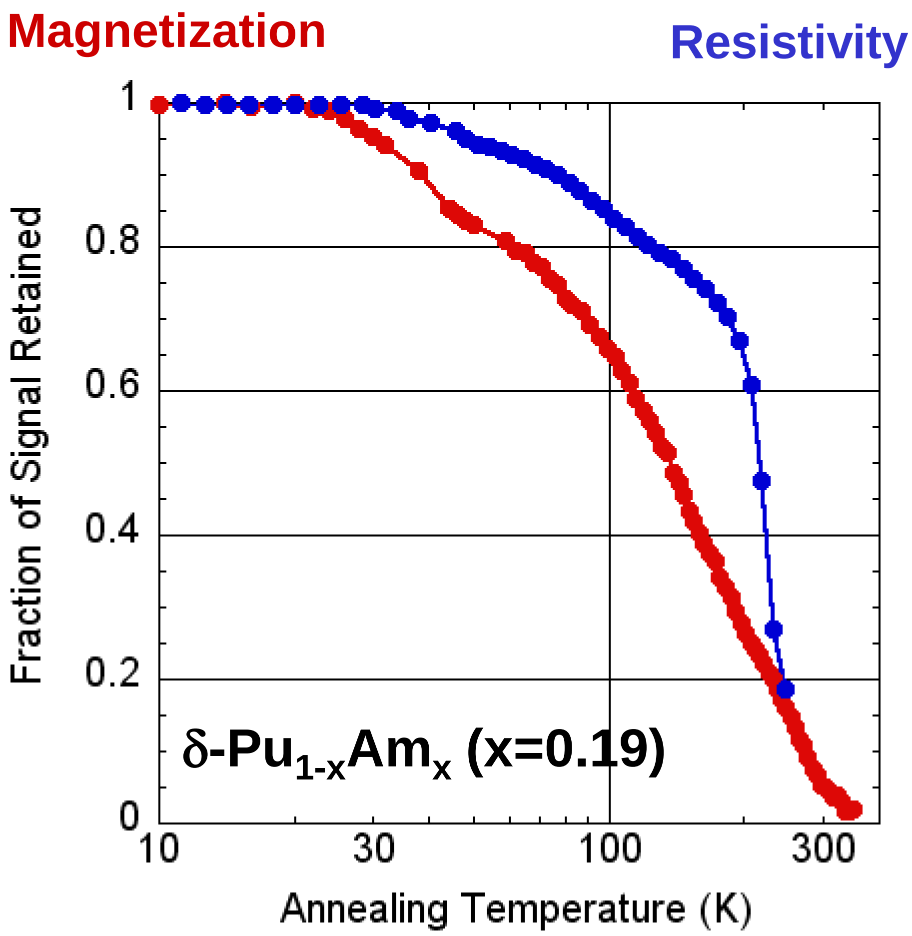

**Bimolecular kinetics are NOT due to interstitial-vacancy close pair recombination**

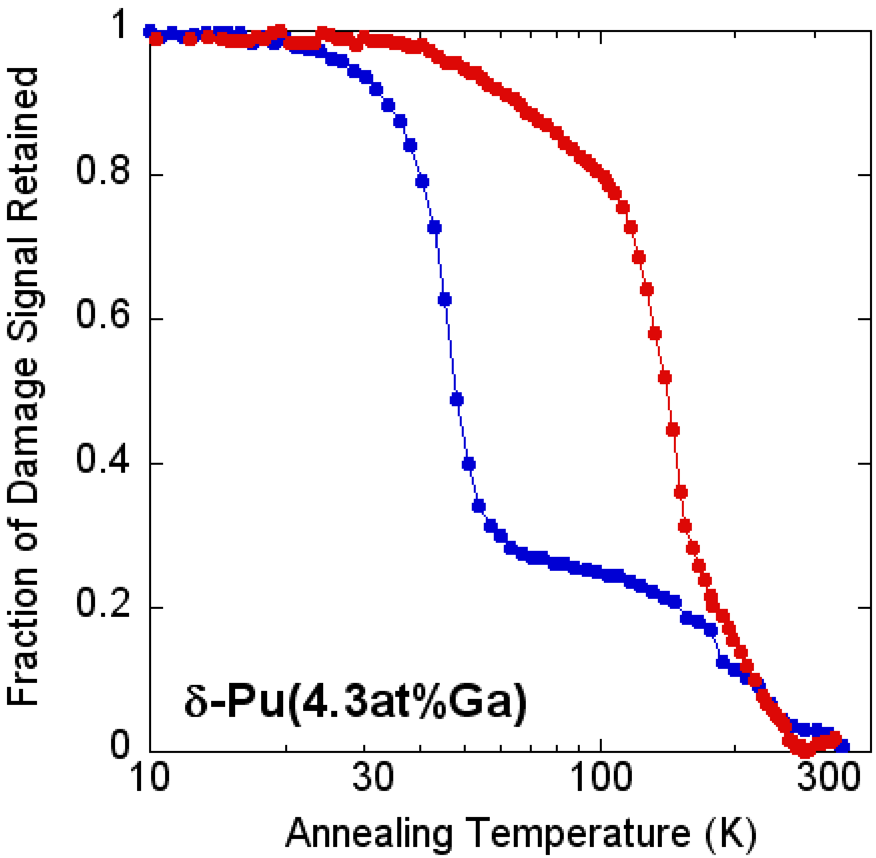
# Isochronal magnetic annealing for different δ-Pu alloys




**Recovery of magnetically observable radiation damage begins at a lower temperature in the expanded lattice**

# Isochronal annealing with two techniques on a PuAm alloy




**The isochronal annealing curves suggest damage structures in PuAm are different from Pu stabilized with Ga**

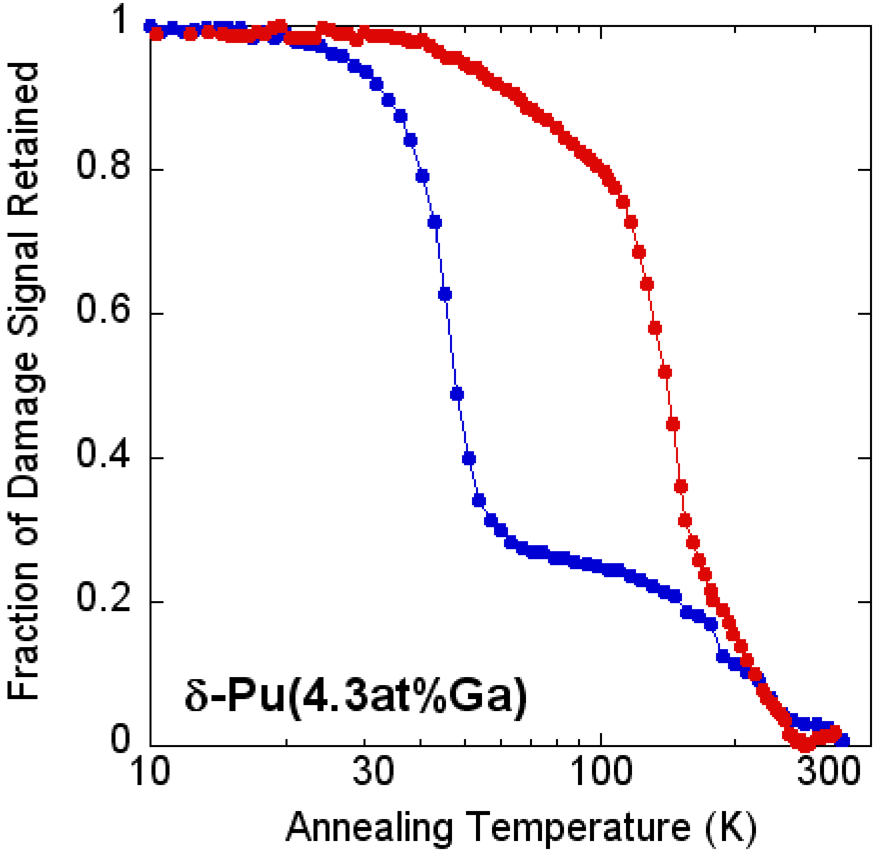
# Conclusions

**The damage cascade due to an 85 KeV U recoil is ~30 nm in diameter**

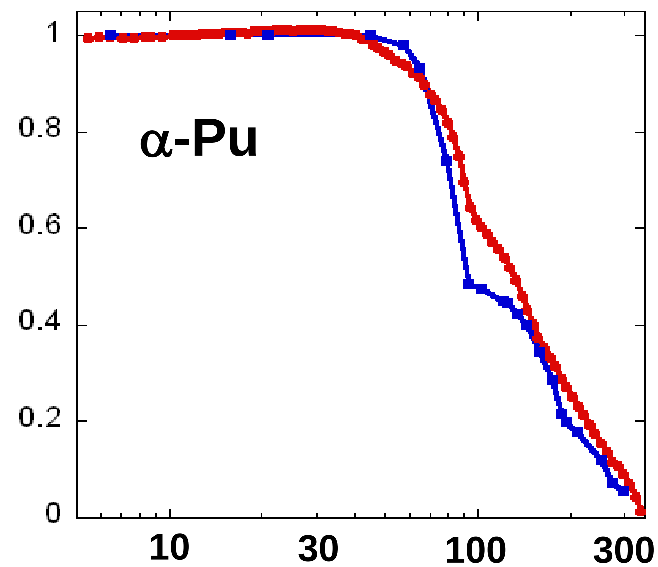
- **Experimental result:**
  - **Magnetization data – a bulk measurement**
- **Theoretical MD simulation:**
  - **Detailed MEAM potential calculations**

**The initial annealing stage follows 2$^{nd}$ order chemical kinetics**

- **Might suggest interstitial-vacancy close pair recovery**
  - **Not consistent with proton irradiation studies**
- **Isochronal Magnetic annealing suggests vacancy annihilation limited below Stage III**
- **Interstitial clustering? Interstitial-impurity trapping?**



Fraction of Damage Signal Retained
1
0.8
0.6
0.4
0.2
0
10
30
100
300
Annealing Temperature (K)
δ-Pu(4.3at%Ga)

1
0.8
0.6
0.4
0.2
0
10
30
100
300
α-Pu